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The synthesis and properties of $[Fe_3(CO)_{11}(RCN)]$ derivatives, and a high-yield general route to mono- and di-substituted derivatives of $[Fe_3(CO)_{12}]$; the crystal and molecular structure of $[Fe_3(CO)_{11}(NCC_6H_4\text{-2-Me})]$ *

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Abstract

The clusters $[Fe_3(CO)_{11}(RCN)]$ (**1**: R = Me, C_3H_5, C_6H_5, or C_6H_4-2-Me) have been prepared at low temperature from $[Fe_3(CO)_{12}]$ and RCN in the presence of Me_3NO. Compounds **1** react essentially quantitatively with a wide range of two-electron donors, L, (viz.: CO, PPh_3, $P(OMe)_3$, PPh_2H, PPh_2Me, PF_3, CyNC (Cy = cyclohexyl), $P(OEt)_3$, $SbPh_3$, PBu_3, $AsPh_3$, or SnR_2 (R = $CH(SiMe_3)_2$)) to give $[Fe_3(CO)_{11}L]$ (**2**). In some cases (**2**), on treatment with Me_3NO and then L′ (L′ = a second two-electron donor) yields $[Fe_3(CO)_{10}LL']$ in high yield.

The crystal and molecular structures of **1** (L = NCC_6H_4Me-2) have been determined by a full single crystal structure analysis, and shown to have an axial nitrile coordinated at the unique iron atom, with two CO groups bridging the other two metal atoms.

Introduction

Organic nitriles usually bond to clusters as η^1-N ligands, in which mode they are generally labile. This lability has been employed for the activation of carbonyl clusters, in which the mean M–M and M–C bond strengths may be comparable [1,2]. The procedure has been particularly successful with the dodecacarbonyls of ruthenium and osmium [2]. Furthermore, we have reported reactions of $[SnR_2]$ (R = $CH(SiMe_3)_2$) with $[M_3(MeCN)_n(CO)_{12-n}]$ (M = Ru, $n = 0$, 1 or 2; M = Os, $n = 1$ or 2) to yield the mixed metal clusters $[M_3(SnR_2)_n(CO)_{12-n}]$ [3].

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* This paper is dedicated to Professor Colin Eaborn, F.R.S., to mark the occasion of his 65th birthday, with the heartfelt good wishes of the authors.

For iron, however, $[Fe_3(CO)_{12}]$ gives diiron derivatives [3], while σ-bonded nitrile derivatives $[Fe_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$ or 2) were unknown, although μ_3-benzonitrile triiron complexes have been prepared [4], and $[Fe_3(\mu_3\text{-PPh})_2(CO)_7(NCMe)_2]$ has been characterised [1]. We therefore sought a route to simple triiron derivatives, and report now on the synthesis of a series of derivatives $[Fe_3(CO)_{11}(NCR)]$ (**1**: R = Me, C_3H_5, C_6H_5 or C_6H_4-2-Me) and their reactions with electron-pair donors. The structure of one of the derivatives (**1**: R = C_6H_4-2-Me) has been determined by a full single crystal structure analysis, reported here. The synthesis of the mixed metal clusters has been reported, in part elsewhere [3].

Results and discussion

Preparation and properties of the nitrile derivatives

When a solution of $[Fe_3(CO)_{12}]$ and RCN in CH_2Cl_2 is treated at low temperature with Me_3NO, the mononitrile derivative $[Fe_3(CO)_{11}(NCR)]$ (**1**) is produced in excellent yield (eq. 1). No apparent colour change occurs in the dark green

$$[Fe_3(CO)_{12}] + RCN + Me_3NO \xrightarrow[-50\,^\circ C]{CH_2Cl_2} [Fe_3(CO)_{11}(NCR)] + CO_2 + Me_3N \qquad (1)$$

$$(\mathbf{1}\text{: R} = \text{Me, } C_3H_5\text{, Ph or } C_6H_4\text{-2-Me})$$

solution, but both the consumption of $[Fe_3(CO)_{12}]$ and the appearance of **1** can be conveniently monitored by TLC. Addition of excess RCN and Me_3NO is necessary for reasonably rapid conversion of $[Fe_3(CO)_{12}]$ to **1**, but no further substitution occurs. If solutions of **1a**–**1d** are warmed at this stage (i.e., in the presence of an excess of RCN), they react to give an extremely dioxygen sensitive, deep-red solution (removal of the solvent from the solutions under vacuum results in further decomposition). The nitrile derivatives **1** may be isolated by filtration through a short silica column (removing Me_3NO), followed by evaporation of the solvent and the excess of RCN under vacuum, both at low temperature. Compounds **1**, together with relevant data for characterization, are detailed in Table 1.

Reactions of 1 with donor ligands

The nitrile ligands of **1** are rapidly displaced by a variety of two-electron donor ligands, L, at low temperatures, followed by warming to room temperature (eq. 2) (For L, see Table 2).

$$\underset{(\mathbf{1})}{[Fe_3(CO)_{11}(NCR)]} + L \xrightarrow[-50\,^\circ C]{CN_2Cl_2} \underset{(\mathbf{2})}{[Fe_3(CO)_{11}L]} + RCN \qquad (2)$$

Although compounds **1** all undergo nitrile displacement readily, **1a** or **1b** are preferred for immediate conversion to **2** because of the ease of removal of the volatile RCN. This reaction, with appropriate L, results in high yields of pure **2**, and therefore is the preferred route for their preparation. The reaction of **1** with carbon monoxide, at room temperature, results in rapid, quantitative conversion to $[Fe_3(CO)_{12}]$. Thus **1a** is presumably the intermediate in the reported synthesis of ^{13}CO-enriched $[Fe_3(CO)_{12}]$ [5]. The compounds **2**, together with relevant characterization and spectroscopic data, are detailed in Table 2.

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Table 1

Characterization of $[Fe_3(CO)_{11}(NCR)]$

	R	Yield (%)	M.p. (°C)	IR [a] ν(CO) (cm^{-1})	^1H NMR [b] δ(ppm)	^{13}C NMR [b] δ(ppm)	MS M^+ (m/z)	Analysis (Calcd. (Found)(%))		
								C	H	N
1a	Me	92	40(dec)	2085m, 2038s, 2030s, 2010s, 1998s, 1990sh, 1968m, 1950m, 1845br, 1805br	2.55(s) [c]	215(s), 132.09(s), 4.52(s) [c]				
1b	C_3H_5	88	40(dec)	2080m, 2025sh, 2015s, 1995s, 1985s, 1975sh, 1960sh, 1845m,br, 1805m,br						
1c	Ph	80	50(dec)	2080m, 2035sh, 2020s, 2005sh, 1992s, 1982s, 1975sh, 1958m, 1948m, 1843m, 1805m, 1790m	7.65(m) [d]		579	37.35 (35.17)	0.82 (0.81)	2.42 (2.22)
1d	C_6H_4-2-Me	88	50–55(dec)	2080m, 2045sh, 2030s, 2018s, 1993s, 1978sh, 1972m, 1953m, 1840br	2.57(s,3H) 7.38(m,4H)		593	38.49 (37.46)	1.19 (1.12)	2.36 (2.22)

[a] KBr disc; m, medium; s, strong; br, broad; sh, shoulder. [b] Shifts (ppm) are downfield from internal TMS; (m), multiplet; (s). singlet. [c] In CD_2Cl_2. [d] In $CDCl_3$.

Table 2

Characterization and spectroscopic data for $[Fe_3(CO)_{11}L]$ and $[Fe_3(CO)_{10}\{P(OMe_3\}_2]$

L	Yield (%)	M.p. (° C)	Analysis (Calcd. (Found)(%))		R_f [a]	^1H NMR [b,d] δ(ppm)	^{31}P NMR [c,d] δ(ppm)	MS [e] m/z	IR [f] ν(CO) (cm^{-1})
			C	H					
[Fe$_3$(CO)$_{11}$L]									
PPh_3	93	105–108(dec)	47.2 (46.0)	2.04 (2.00)	0.71	7.46(m),7.4(m) (isomers)	–	738 [g]	2080s,2038sh,2020s, 2018sh,2000sh,1993s, 1978s,1955sh,1948s, 1930sh,1833m,br, 1810m,br,1790m,br.
PPh_2Me	90	90–92	42.6 (42.3)	1.94 (1.98)	0.65	2.08(d,3H, J 8.54 Hz), 7.45(m,10H)	33.16(s)	676 [g]	2083s,2010s,1995sh 1980s,1960sh, 1940sh,br,1820br, 1780m,br.
PPh_2H	88	85–86	41.7 (41.3)	1.67 (1.66)	0.63	6.2(d,1H, J 364 Hz) 7.47(m,10H)	40.54(d, J 366 Hz)	662 [h]	2080s,2025s,2005s, 1995s,1980sh,1970s, 1825m,br,1775m,br.
PBu_3	85	oil	40.7 (40.0)	4.00 (3.97)	0.79	1.41(s,2H) 1.60(s,2H) 1.71(s,2H)	34.34(m) 55.5(m) (isomers, J unresolved)	–	2083s,2025s,2005s, 1980sh,1935m,br, 1860m,br,1835m,br, 1800m,br.
$AsPh_3$	88	105–112(dec)	44.5 (44.2)	1.93 (1.85)	0.68	7.44(m)	–	783 [g]	2080m,2025sh,2020s, 1990s,1980sh,1975s, 1965sh,1950s,1830m,br, 1810m,br,1790m,br.
$SbPh_3$	85	100(dec)	42.0 (44.2)	1.82 (1.76)	0.70	7.46(m)	–	828 [g]	2080m,2030sh,2020s 2000sh,1990s,1985sh,, 1975m,1955sh,1948m, 1847m,br,1815m,br, 1787m,br.

P(OMe)$_3$	87	66–67	28.0 (27.6)	1.51 (1.42)	0.61	3.76(d, J 11.3 Hz)	159.9(dc, J 11.9 Hz)	600 [h]	2085s,2025s,2010s, 1997s,1985sh,1970sh, 1837m,br,1800m,br.
P(OEt)$_3$	92	57–58	31.8 (31.7)	2.35 (2.32)	0.60	1.33(t,3H, J 6.83 Hz) 4.08(qn [i],2H, J_{app} 7.1 Hz)	154.2(st, J 7.3 Hz)	642 [g]	2080m,2020sh,2003s, 1985sh,br,1840br, 1805br.
CyNC [j]	88	119–123(dec)	37.0 (36.5)	1.89 (1.59) [k]	0.63	1.71(m,10H) 4.07(s,1H)	–	529 (M – 2CO)$^+$	2083s,2045sh,2025s, 2000s,1985s,1975sh, 1960sh,1845br, 1807br. ν(CN) 2185s.
PF$_3$	97	130–132(dec)	23.4 (23.8)	10.1 [l] (9.75)	0.00	–	158.3(q, J 1352.5 Hz)	–	2100m,2060sh,2050s, 2030sh,2010s,1997sh, 1990sh,1865m,br, 1825m,br, ν(PF) 890sh, 875m.
dppe [m]	75	–	42.7 (43.6)	1.8 (2.0)	0.60	– [n]	– [n]	–	2085s,2020s,2000s, 1990sh,1830m,br, 1795m,br.
[Fe$_3$(CO)$_{10}${P(OMe)$_3$}L]									
PPh$_3$	83	–	44.5 (44.3)	2.90 (2.81)	0.52	3.7(d,9H,J 11 Hz) 7.43(m,15H),	161.7(dc) 181.5(s)	834	2050m,1997sh,1980s,1970sh, 1960s,1950sh,1935sh,1885w, 1875w,1840sh,br,1810sh, 1790m,br.
P(OEt)$_3$	86	–	30.9 (30.7)	3.27 (3.21)	0.56	1.3(t,3H,J 6.83 Hz) 3.71(d,3H,J 11.23 Hz) 4.05(qn [i],2H,J_{app} 7.08 Hz) [o,p]	158.3(st) 163.8(dc)	738	2060m,2010s,1987s,1950sh, 1940sh,1820m,br,1782m,br.

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[a] R_f values measured on silica plates using hexane (55%), CH_2Cl_2 (40%) and MeCN (5%); for [$Fe_3(CO)_{12}$] and [$Fe_3(CO)_{11}$(MeCN)], the R_f values are 0.84 and 0.60, respectively. [b] Measured in $CDCl_3$; δ is downfield from internal TMS. [c] Measured in $CDCl_3$; δ is downfield from external 85% phosphiric acid. [d] s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; st, septet; dc, decet; m, multiplet. [e] Only M^+ is quoted, unless otherwise stated. [f] KBr disc; m, medium; s, strong; br, broad; sh, shoulder. [g] FAB spectrum. [h] EI spectrum. [i] Two overlapping quartets, appearing as a quintet. [j] Cy = cyclohexyl. [k] N: found, 2.4; calcd. 2.39%. [l] Data are for fluorine, not hydrogen. [m] Complex [{$Fe_3(CO)_{11}$}$_2$(dppe)]. [n] Possible isomers complicate the NMR spectra. [o] Apparent. [p] Overlapping quartets.

Table 3

Selected bond lengths (Å) and angles (°) for [$Fe_3(CO)_{11}(NCC_6H_4Me\text{-}2)$]

Bond lengths (Å)		Bond angles (°)	
Fe(1)–Fe(1′)	2.551(0.004)	C(1)–Fe(1)–Fe(3)	79.7(0.5)
Fe(1′)–Fe(3)	2.831(0.007)	C(2)–Fe(1)–Fe(3)	174.3(0.5)
Fe(3)–Fe(1)	2.788(0.007)	C(2)–Fe(1)–C(1)	94.7(0.7)
C(1)–Fe(1)	1.759(0.015)	C(3)–Fe(1)–Fe(3)	86.0(0.7)
C(2)–Fe(1)	1.739(0.016)	C(3)–Fe(1)–C(1)	98.8(0.8)
C(3)–Fe(1)	1.753(0.023)	C(3)–Fe(1)–C(2)	96.3(0.8)
C(10)–Fe(1)	2.185(0.027)	C(10)–Fe(1)–Fe(3)	103.3(0.8)
C(10)–Fe(1′)	1.900(0.027)	C(10)–Fe(1)–C(1)	162.5(0.8)
C(11)–Fe(1′)	1.901(0.024)	C(10)–Fe(1)–C(2)	81.6(0.9)
C(11)–Fe(1)	1.850(0.024)	C(1)–Fe(1)–C(3)	98.6(1.0)
C(7)–Fe(3)	1.783(0.030)	C(11)–Fe(1)–Fe(3)	79.0(0.8)
C(8)–Fe(3)	1.835(0.033)	C(11)–Fe(1)–C(1)	86.67(0.8)
N–Fe(3)	1.970(0.020)	C(11)–Fe(1)–C(2)	99.38(0.9)
C(9)–Fe(3)	1.729(0.027)	C(11)–Fe(1)–C(3)	162.91(1.0)
O(1)–C(1)	1.162(0.015)	C(11)–Fe(1)–C(10)	77.12(1.1)
O(2)–C(2)	1.156(0.017)	C(7)–Fe(3)–Fe(1)	155.0(1.0)
O(3)–C(3)	1.174(0.023)	C(8)–Fe(3)–Fe(1)	105.2(1.0)
O(7)–C(7)	1.266(0.038)	C(8)–Fe(3)–C(7)	99.2(1.2)
O(8)–C(8)	1.171(0.045)	N–Fe(3)–Fe(1)	93.5(0.6)
C(12)–N	1.140(0.024)	N–Fe(3)–C(7)	90.7(1.1)
C(9)–O(9)	1.191(0.030)	N–Fe(3)–C(8)	92.8(1.1)
C(11)–O(11)	1.230(0.051)	C(9)–Fe(3)–Fe(1)	82.9(0.9)
C(10)–O(10)	1.162(0.026)	C(9)–Fe(3)–C(7)	91.8(1.3)
C(13)–C(12)	1.379(0.028)	C(9)–Fe(3)–C(8)	89.9(1.3)
C(19)–C(14)	1.340(0.049)	C(9)–Fe(3)–C(8)	89.9(1.3)
		C(9)–Fe(3)–N	176.0(1.1)
		O(1)–C(1)–Fe(1)	176.9(1.3)
		O(2)–C(2)–Fe(1)	178.0(1.5)
		O(3)–C(3)–Fe(1)	165.3(2.0)
		O(7)–C(7)–Fe(3)	170.4(2.7)
		O(8)–C(8)–Fe(3)	165.1(3.3)
		C(12)–N–Fe(3)	175.5(2.1)
		C(12)–N–O(11)	173.4(2.7)
		O(10)–C(10)–Fe(1)	136.3(2.3)
		O(9)–C(9)–Fe(3)	171.2(1.7)
		O(11)–C(11)–Fe(1)	141.2(3.3)
		Fe(1)′–Fe(1)–C(10)	46.5(8)
		Fe(1)′–Fe(1)–C(11)	48.0(8)
		Fe(1)–Fe(1′)–C(10)	56.6(8)
		Fe(1)–Fe(1′)–C(11)	46.3(8)
		Fe(1)–C(10)–Fe(1′)	76.9(8)
		Fe(1)–C(11)–Fe(1′)	85.7(8)
		Fe(1′)–C(10)–O(10)	145.2(2.3)
		Fe(1′)–C(11)–O(11)	132.5(3.3)
		C(13)–C(12)–N	174.6(3.4)
		C(18)–C(13)–C(12)	117.4(1.3)
		C(14)–C(13)–C(12)	122.6(1.3)
		C(19)–C(14)–C(15)	117.8(2.0)
		C(19)–C(14)–C(13)	122.0(2.0)

Preparation of the compounds [$Fe_3(CO)_{10}LL'$]

Compounds **2** vary in their potential to undergo further substitution with Me_3NO/NCR. For example, **2** ($L = PF_3$) is inert to Me_3NO attack, whereas **2** ($L = P\{OMe\}_3$) may be converted into $[Fe_3(CO)_{10}\{P(OMe)_3\}L']$ in high yield, as shown in eq. 3.

$$[Fe_3(CO)_{11}\{P(OMe)_3\}] \xrightarrow[CH_2Cl_2,\ -60\,^\circ C]{Me_3NO,\ MeCN} [Fe_3(CO)_{10}\{P(OMe_3)\}(NCMe)]$$

$$\xrightarrow[CH_2Cl_2,\ -40\,^\circ C]{L'} \begin{array}{l}[Fe_3(CO)_{10}\{P(OMe)_3\}L'] \\ (L' = PPh_3 \text{ or } P(OEt)_3)\end{array} \qquad (3)$$

In an attempt to effect further substitution, $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OEt)_3\}]$ was treated with Me_3NO in the presence of MeCN, but the disubstituted carbonyl was unreactive, even in boiling dichloromethane. The spectroscopic and characterization data for $[Fe_3(CO)_{10}\{P(OMe)_3\}L]$ are given in Table 2.

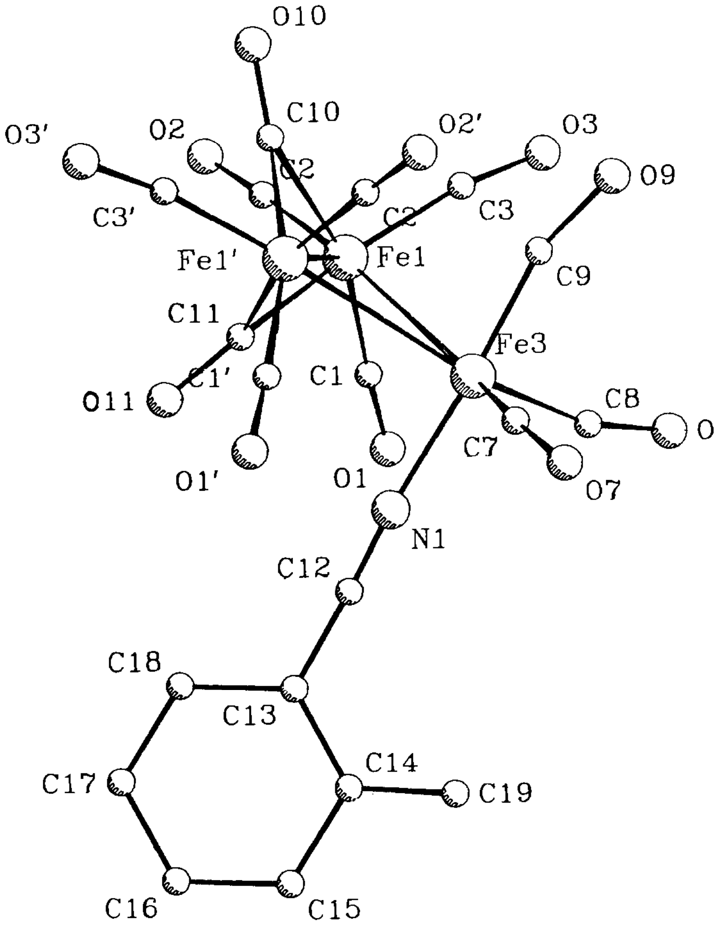

Fig. 1. A single molecule of **1d** showing the numbering scheme. The two-fold axis runs vertically (as drawn) through the mid point of the Fe(1)–Fe(1′) vector.

Structure of [$Fe_3(CO)_{11}(NCC_6H_4$-2-Me)] (1d)

1d is the first [$Fe_3(CO)_{11}$(NCR)] species to be structurally characterised, although nitrile substituted iron clusters having either bridging phosphorus ligands [1] or bridging nitriles [4] have been studied. The compound **1d** has a single nitrile ligand axially coordinated to the unique iron atom, with two asymmetrically bridging carbonyls spanning the other metal atoms (See Fig. 1). In this respect, it resembles one isomer of [$Fe_3(CO)_{11}(PPh_3)$] [6]. The degree of asymmetry in the carbonyl bridges lies between that found in the analogous isomer of the triphenylphosphine derivative [6], and that in [$Fe_3(CO)_{12}$] [7,8], being slightly lower than for the latter. A further feature is the lengthening observed for the two Fe–Fe bonds to the unique iron, of about 0.1 Å compared to [$Fe_3(CO)_{12}$]. This lengthening probably illustrates the bond weakening effect associated with the relatively poor π-acceptor nitrile ligand. Other aspects of the molecular geometry are quite normal. Selected bond lengths and angles are given in Table 3.

Experimental

The experimental techniques used and the instrumentation employed have been described previously [9]. Characterisation data and yields are given in Tables 1 and 2.

*Preparation of [$Fe_3(CO)_{11}$(NCR)], (**1a**, R = Me or **1b**, R = allyl)*

[$Fe_3(CO)_{12}$] (0.25 g, 0.493 mmol) and RCN (4 cm^3, 76.5 mmol (R = Me), 49.7 mmol (R = allyl)) were dissolved in dry, degassed dichloromethane (150 cm^3), and the resulting stirred solution was cooled under an atmosphere of dinitrogen to −40 ° C. An excess of freshly sublimed trimethylamine *N*-oxide (tmno; ca. 0.1–0.2 g) was added, and the mixture allowed to warm slowly to −15 ° C. The reaction was monitored by TLC (See Table 2). Any remaining [$Fe_3(CO)_{12}$] was removed by further small additions of tmno (ca. 0.01 g), holding the temperature in the range −15 to −5 ° C. Care must be taken not to allow the temperature to rise above 0 ° C at this stage. The resulting solution was cooled to −50 ° C, and quickly flashed (eluant: dichloromethane) through a short (5 cm) silica column under argon, to remove excess tmno. Solvent and excess RCN were removed under vacuum, keeping the product at −20 ° C, to give a black solid. Recrystallisation from degassed hexane or toluene (ca. −27 ° C) afforded black-green needles.

*Preparation of [$Fe_3(CO)_{11}$(NCR)], (1c, R = Ph or **1d**, R = C_6H_4-2-Me)*

The above method was followed except that only ca. a ten-fold molar excess of nitrile was employed, to minimise subsequent decomposition. Following the flash chromatography, at −20 ° C, roughly half the solvent was removed in vacuum; dry, degassed hexane (200 cm^3) was added, and a further 100 cm^3 of the solvent mixture removed under vacuum at the same temperature. The resulting solution (predominantly hexane as solvent) was set aside in the freezer (−27 ° C) to give a black-green crystalline product.

Preparation of [$Fe_3(CO)_{11}$L] (For L, see Table 2)

To a stirred solution of [$Fe_3(CO)_{11}$(NCMe)] (0.5 g, 0.96 mmol) in dichloromethane (200 cm^3) was added L (1.45 mmol) at −50 ° C. After consumption of the starting nitrile complex (TLC), the mixture was allowed to warm to −20 °C, and volatiles removed under vacuum at this temperature. The resulting black-green solids were recrystallised from dry, degassed hexane under dinitrogen at −27 °C.

NB: In the case of L = PF_3, the gas was bubbled through a solution of **1a** in dichloromethane at 0 °C, the reaction being completed (TLC, propanone as eluant) at room temperature.)

Preparation of $[Fe_3(CO)_{10}\{P(OMe)_3\}L']$ *(L′ = PPh_3 or $P(OEt)_3$)*

A solution of $[Fe_3(CO)_{10}\{P(OMe)_3\}(NCMe)]$ was prepared as for $[Fe_3(CO)_{11}(NCMe)]$, but using $[Fe_3(CO)_{11}\{P(OMe)_3\}]$ in place of $[Fe_3(CO)_{12}]$. The resulting solution was treated at −40 °C with a slight molar excess of L′. The mixture was allowed to warm to −30 °C, when the reaction was complete (TLC). About half the solvent was removed under vacuum at −20 °C, and heptane (110 cm^3) added. Volatiles were again removed to leave predominantly heptane as solvent, and the mixture set aside (−27 °C) to crystallise. Dark green crystals were obtained.

Crystal data. $C_{19}H_7NO_{11}Fe_3$; $M = 578.799$, monoclinic, space group $C2/c$; a 7.748(1), b 24.855(2), c 12.300(2) Å, β 107.62(1)°; u 2257.66 Å^3; D_c 1.70 g cm^{-3}, $Z = 4$; $F(000) = 588$, $\mu(\text{Mo-}K_\alpha)$ 10.46 cm^{-1}.

Table 4

Atomic coordinates for $[Fe_3(CO)_{11}(NCC_6H_4Me\text{-}2)]$

Atom	x	y	z
Fe(1)	0.0537(3)	−0.1038(1)	0.3588(2)
Fe(3)	−0.2566(9)	−0.1638(3)	0.2555(6)
C(1)	0.0998(20)	−0.1620(6)	0.4439(12)
C(2)	0.2568(22)	−0.0722(6)	0.4299(13)
C(3)	−0.0793(30)	−0.0693(9)	0.4288(18)
C(7)	−0.4403(41)	−0.1867(11)	0.1386(23)
C(8)	−0.3319(42)	−0.1895(12)	0.3736(25)
N	−0.1189(25)	−0.2297(7)	0.2491(16)
O(1)	0.1262(15)	−0.1995(4)	0.5032(9)
O(2)	0.3944(19)	−0.0523(5)	0.4760(11)
O(3)	−0.1505(24)	−0.0539(7)	0.4947(15)
O(7)	−0.5800(44)	−0.2068(13)	0.0682(27)
O(8)	−0.3909(54)	−0.1942(15)	0.4522(33)
O(9)	−0.4551(27)	−0.0658(6)	0.2689(19)
O(11)	0.2473(75)	−0.1736(17)	0.2453(48)
O(10)	0.0796(25)	0.0029(7)	0.2292(15)
C(10)	0.0543(38)	−0.0432(11)	0.2301(24)
C(9)	−0.3642(34)	−0.1034(10)	0.2610(21)
C(11)	0.1280(34)	−0.1424(9)	0.2526(21)
C(12)	−0.0444(32)	−0.2694(8)	0.2502(27)
C(15)	0.0628(33)	−0.4143(7)	0.2507(25)
C(16)	0.2238(33)	−0.4117(7)	0.2223(25)
C(17)	0.2925(33)	−0.3619(7)	0.2030(25)
C(18)	0.2001(33)	−0.3148(7)	0.2121(25)
C(13)	0.0392(33)	−0.3172(7)	0.2405(25)
C(14)	−0.0295(33)	−0.3672(7)	0.2598(25)
C(19)	−0.1905(66)	−0.3719(17)	0.2785(40)

Data collection and structure solution

A black needle-shaped crystal of approximate size 0.1 × 0.1 × 0.4 mm^3 was mounted on a Stoe four-circle diffractometer and the intensities of 1651 reflections in the range $2.5 < \theta < 22.5°$ measured using Mo-K_α radiation (graphite monochromator). The data were reduced to give 1520 unique reflections (merging $R = 0.0299$) of which 1050 had $|F_{obs}| > 4\sigma(F_{obs})$ and were used in the structure solution and refinement.

With the iron atoms anisotropic, a rigid benzene ring geometry, and all hydrogen atoms in calculated positions, refinement converged at 0.0821. The model used treats the unique iron atom and associated ligands as disordered about the twofold axis. This gives an entirely satisfactory convergence and molecular geometry, although at the crystallographic level there are short intermolecular contacts to carbonyls on the unique iron. Because of these short contacts, the assignment of the space group as *C*2/*c* cannot be correct. However, examination of the structure solution from data reduction to final refinements, in both *C*2/*c* and *Cc*, indicates that the crystal was probably twinned, and that a completely satisfactory refinement with these data is not possible. The best model for the molecular structure appears to be *C*/*c*; refinement in the non-centrosymmetric space group gave unreasonable bond parameters.

The final structure is shown in Fig. 1. Selected bond lengths and angles are shown in Table 3, and atomic coordinates of nonhydrogen atoms in Table 4. The data have been deposited with the Cambridge Crystallographic Data Centre.

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